Sensitivity of the isotopologues of hydronium to variation of the electron-to-proton mass ratio

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We study the sensitivity of the microwave and submillimeter transitions of the isotopologues of hydronium to the variation of the electron-to-proton mass ratio μ. These sensitivities are enhanced for the low frequency mixed inversion-rotational transitions. The lowest frequency transition (6.6 GHz) takes place for isotopologue H_2DO^+ and respective sensitivity to μ-variation is close to 200. This is about two orders of magnitude larger than the sensitivity of the inversion transition in ammonia, which is currently used for the search of μ-variation in astrophysics.

I. INTRODUCTION.

The search for the possible variation of fundamental constants is a poor man's way to look for physics beyond the Standard Model. There are two main approaches to such studies. First is to make laboratory measurements with different atomic and molecular clocks in order to look for local variations on the time scale of the order of a year. Second is to compare laboratory measurements with astrophysical observations, where one can study variations on a much bigger space and time scale up to 10 billion years. Advantage of the first approach is in unprecedented accuracy of experiments with atomic clocks. On the other hand, the second approach allows exploring bigger scales and different environments. For example, the local matter density in the laboratory experiments and in interstellar molecular clouds differ by more than 10 orders of magnitude. We can conclude that these two approaches are complementary to each other [1]. In this paper we do not discuss laboratory experiments and focus on astrophysical applications.

In astrophysics all frequency shifts with respect to the laboratory values are conventionally interpreted as Doppler shifts, $\Delta\omega/\omega = V/c$, where V is the line of sight velocity of the object and c is the speed of light. However, if we observe several lines from the same object, we can study (small) velocity offsets between them. In the search for the variation of fundamental constants we look for the correlation between these offsets and sensitivities of the observed transitions to the variation to fundamental constants.

It is now well known that the tunneling transition in ammonia is highly sensitive to the electron-to-proton mass ratio $\mu = m_e/m_p$ [2]. This transition is often observed from the interstellar dark molecular clouds in our Galaxy. Comparison of the apparent Doppler shift for this transition with those of rotational transitions of other molecules provides a very sensitive test for the dependence of the mass ratio μ on the local matter density [3–5]. Moreover, ammonia was detected in two high redshift objects with $z = 0.68$ and $z = 0.89$. That allows to place the most stringent present limits on μ-variation on a cosmological time scale [6–9].

Because all observed ammonia transitions have the same sensitivity to the variation of the fundamental constants, one has to use rotational transitions in *other* molecules as a reference. This can lead to the systematic effects caused by different spacial distribution of the molecules in gas clouds (so called Doppler noise) [10]. Therefore, it is desirable to find molecules, where one can simultaneously observe several lines with high *and* different sensitivities to μ-variation. In this case the Doppler noise is minimized because all lines are observed from the same gas. By now we know several such molecules, including OH [11, 12] and CH [13], partly deuterated ammonia [14], hydronium ion (H_3O^+) [15], and methanol (CH_3OH) [16, 17]. These molecules often have higher sensitivity than ammonia and can be used as independent source of information on variations of fundamental constants.

In this paper we consider the hydronium isotopologues H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+. Like ammonia, hydronium also has a double minimum vibrational potential. The inversion transitions occur when the oxygen nucleus tunnels through the plane of the hydrogen/deuterium nuclei. This leads to an inversion splitting of the rotational levels. The splitting in H_3O^+ is very large, about 55 cm^{-1}, as compared to the 0.8 cm^{-1} splitting in NH_3. Because of that the inversion transition is effectively mixed with rotational transitions and the inversion-rotational spectrum of hydronium is observed in the submillimeter-wave region. Here we show that all hydronium isotopologues have mixed transitions with high sensitivity to μ-variation and we also give improved estimate of the sensitivity coefficients for the main isotopologue H_3O^+.

II. GENERAL FORMALISM

A. Sensitivity coefficients

The dimensionless sensitivity coefficients to the variation of fundamental constants can be defined as [14]

$$\frac{\delta\omega}{\omega} = Q_\alpha \frac{\delta\alpha}{\alpha} + Q_\mu \frac{\delta\mu}{\mu} + Q_g \frac{\delta g_n}{g_n}. \tag{1}$$

Here $\alpha \approx 1/137.036$ is the fine-structure constant, $\mu = m_e/m_p \approx 1/1836.15$, g_n is the nuclear g-factor, and Q_α, Q_μ, and Q_g are the corresponding sensitivity coefficients. Note that g_n is not a fundamental constant, but it weakly depends on the quark masses [18] and has to be considered as independent parameter whenever magnetic hyperfine structure is involved.

It is known that tunneling and rotational transitions in molecules, built from light elements, are mostly sensitive to μ-variation: $Q_\mu \gtrsim 1$, while $Q_\alpha \ll 1$ and $Q_g \ll 1$. In the following we disregard coefficients Q_α and Q_g and concentrate on calculating the dominant sensitivity coefficient Q_μ. In the next two sections we consider purely inversion transitions. Note, that for the asymmetric isotopologues H_2DO^+ and HD_2O^+ such transitions are not observable; they occur only in combination with rotational transitions ω_r [14]. We will discuss mixed inversion-rotational transitions in Sec. II D.

B. Inversion potential and reduced mass

As explained above, we can link the variation of the inversion transition $\delta\omega_{\rm inv}/\omega_{\rm inv}$ to the variation of the single fundamental constant μ:

$$\frac{\delta\omega_{\rm inv}}{\omega_{\rm inv}} = Q_{\mu,{\rm inv}} \frac{\delta\mu}{\mu}. \tag{2}$$

We can present the Hamiltonian for the inversion process as (if not said otherwise, we use atomic units throughout the paper):

$$H = -\frac{1}{2M} \frac{\partial^2}{\partial x^2} + U(x), \tag{3}$$

where x is the tunneling coordinate and M is the respective reduced mass. For example, x can be the distance from oxygen to the plane of hydrogens. Following [19] we parameterize the potential $U(x)$ as follows

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{2}dx^4 + b\,e^{-cx^2}. \tag{4}$$

Parameters k, b, c, and d can be found by fitting vibrational frequencies for the molecule H_3O^+. As a result we obtained $k = 0.08917$, $b = 0.04977$, $c = 1.36954$, and $d = 0.00138$.

Another way to find the parameters in Eq. (4) is to fit the inversion frequency of the ground vibrational state

and the barrier height. The latter was accurately determined within "semi-empirical" approach in Ref. [20] to be $652.9\,{\rm cm}^{-1}$. In this case we got $k = 0.08907$, $b = 0.04967$, $c = 1.30429$, and $d = -0.00541$. To find the barrier height $\Delta U \equiv U_{\rm max} - U_{\rm min}$ we need to solve equation $dU(x)/dx = 0$. Obviously, $U_{\rm max} = U(0) = b = 10901$ $\rm cm^{-1}$. As to $x_{\rm min}$ and $U_{\rm min}$, we need to solve numerically the equation

$$k + 2d\,x_{\rm min}^2 - 2b\,c\,e^{-cx_{\rm min}^2} = 0\,, \tag{5}$$

which gives $x_{\rm min} = 0.5635$ and $U_{\rm min} = 10248\,{\rm cm}^{-1}$. From this we get $\Delta U \approx 653\,{\rm cm}^{-1}$ in a perfect agreement with the semi-empirical result $652.9\,{\rm cm}^{-1}$ from Ref. [20].

Comparing two sets of parameters we see that they are very close with the exception of the parameter d. We have checked that both sets of parameters for the potential $U(x)$ lead to very close results for the sensitivity coefficients. The numerical results which will be discussed in the following are obtained with the second set.

In order to find eigenvalues of the Hamiltonian (3) we need to know the reduced masses for different isotopologues of hydronium. For the symmetric species H_3O^+ and D_3O^+ three protons (or deuterons) can be treated as a single particle with the mass $m = 3\,m_{p(d)}$. Then the reduced mass for the inversion mode can be found within two simple models.

If we assume that the H–H distances are constant during inversion, then the vibration involves only a change in the distance between the plane of hydrogens and oxygen. The reduced mass $M(H_3O^+)$ can be written as

$$M(H_3O^+) = \frac{3m_p M_O}{3m_p + M_O}, \tag{6}$$

where M_O is the mass of the oxygen nucleus.

Alternatively, we can assume that the H–O distances are constant. Then the inversion coordinate corresponds to the angle and the reduced mass is given by [19]

$$M(H_3O^+) = \frac{3m_p\,(M_O + 3m_p \sin^2\theta)}{3m_p + M_O}. \tag{7}$$

Here θ is the angle between the plane of the hydrogen atoms and an H–O bond. Using the value of the angle, α, between two H–O bonds $\alpha({\rm HOH}) = 111.3°$ [21] we obtain $\theta \approx 17.6°$. To find the reduced mass of the D_3O^+ molecule we only need to change m_p to $m_d \approx 2m_p$ in Eqs. (6) and (7). Considered here models present two limiting cases. The difference between them constitutes only 1.7% for H_3O^+ and 3.4% for D_3O^+. More accurate values for reduced mass should lie between these limits.

The motion of the asymmetric species H_2DO^+ and HD_2O^+ is more complex and finding reduced masses is more difficult. We can consider it as a free parameter that can be found from fitting the theoretical inversion frequency of the ground state to the experimental value. Note that the inversion frequencies of the ground states are measured with high precision for all the molecules H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+ [20].

TABLE I: The reduced masses M, the experimental and theoretical inversion frequencies ω_{inv}, and the numerically calculated sensitivity coefficients $Q_{\mu,\mathrm{inv}}$.

Molecule	M (a.u.)	ω_{inv} (cm^{-1}) Experim.	ω_{inv} (cm^{-1}) Theor.	$Q_{\mu,\mathrm{inv}}$
H_3O^+	4639	55.35	55.79	1.97
	4657		55.35	1.98
	4718		53.94	1.99
H_2DO^+	5419	40.52	40.52	2.15
HD_2O^+	6485	27.03	27.03	2.36
D_3O^+	8012	15.36	15.92	2.65
	8120		15.36	2.67
	8287		14.54	2.70

TABLE II: The reduced masses M, the ground state vibrational energy E_0, the action over classically forbidden region S, and the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$ obtained in the WKB approximation.

Molecule	M (a.u.)	E_0 (cm^{-1})	S	$Q_{\mu,\mathrm{inv}}$
H_3O^+	4639	339	1.36	1.92
	4657	339	1.36	1.91
	4718	337	1.36	1.90
H_2DO^+	5419	322	1.62	2.10
HD_2O^+	6485	302	1.96	2.33
D_3O^+	8012	279	2.45	2.64
	8120	278	2.44	2.63
	8287	276	2.44	2.61

TABLE III: The recommended values of the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$. The uncertainties are given in parentheses.

	H_3O^+	H_2DO^+	HD_2O^+	D_3O^+
$Q_{\mu,\mathrm{inv}}$	2.0(1)	2.2(1)	2.4(1)	2.7(1)

C. Sensitivity coefficient for inversion transition

A numerical integration of the Schrödinger equation with the potential (4) allows us to find eigenvalues of the Hamiltonian and, respectively, to calculate the inversion frequency. Then we can find the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$ by numerical differentiation taking into account that reduced mass M in atomic units scales as μ^{-1}.

In Table I we present the results of the numerical calculations for the ground state inversion frequencies and the sensitivity coefficients for the isotopologues of hydronium. For the symmetric species H_3O^+ and D_3O^+ we present results for three values of the reduced mass. The first and the third values correspond to Eqs. (6) and (7), correspondingly. The second value is found by fitting the ground state tunneling frequency. As seen from the table the coefficients $Q_{\mu,\mathrm{inv}}$ are almost insensitive to these small changes of the reduced masses. Even for the heavier isotopologue D_3O^+ the differences between calculated values of $Q_{\mu,\mathrm{inv}}$ do not exceed 2%.

Another way to find the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$ is based on the semi-classical Wentzel-Kramers-Brillouin (WKB) approximation. A detailed description of this approach and its application to calculations of $Q_{\mu,\mathrm{inv}}$ for different molecules was repeatedly discussed earlier (see, e.g., [6, 14, 15, 22]). For this reason we present here only the main expressions.

Following Landau and Lifshitz [23] we can write the inversion frequency as

$$\omega_{\mathrm{inv}} \approx \frac{2E_0}{\pi} e^{-S}, \qquad (8)$$

where S is the action over classically forbidden region and E_0 is the ground state vibrational energy calculated from the bottom of the well $U_{\min}$. Harmonic approximation $2E_0 = \omega_v$ (ω_v is experimentally observed vibrational frequency) is not applicable to hydronium and E_0 has to be found by solving Eq. (3) numerically. After that using the experimentally known ω_{inv} we can obtain the action S from Eq. (8).

It was shown in [6, 15] that the sensitivity coefficient

$Q_{\mu,\mathrm{inv}}$ can be expressed through S, E_0, and ΔU as follows

$$Q_{\mu,\mathrm{inv}} \approx \frac{1+S}{2} + \frac{S\,E_0}{2(\Delta U - E_0)} . \qquad (9)$$

The third term in Eq. (9) was first obtained in Ref. [6]. It was shown there that the numerical factor for this term depends on the form of the potential barrier. (It is worth mentioning that there is a typo in Eq.(12) of [6]: the coefficient $1/4$ should read as $1/2$.) The square and triangular potential barrier were considered. For both of them the coefficients in front of the third term were calculated and the average was taken. This average value is reproduced in Eq. (9). Here we considered a more realistic, parabolic form of the potential barrier and found, that solution for this case exactly coincides with Eq. (9).

Knowing the values of S, E_0, and ΔU we can calculate the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$ in the WKB approximation. The results are presented for all molecules in Table II. The WKB approximation is known to work well for $S \gg 1$. As seen from Table II, for hydronium S is close to unity. For this reason we cannot anticipate high accuracy for the sensitivity coefficients obtained in this approximation. Nevertheless, comparing the results of Tables I and II, we see a reasonable agreement between the numerical and semi-classical values of $Q_{\mu,\mathrm{inv}}$. The largest discrepancy does not exceed 5%. Based on the comparison of all approximations, considered here, we present the recommended values of the sensitivity coefficients $Q_{\mu,\mathrm{inv}}$ in Table III. We estimate the accuracy of our calculations to be not worse than 5%.

The coefficient $Q_{\mu,\mathrm{inv}}$ for H_3O^+ calculated in this work differs by approximately 20% from that in [15]. In Ref. [15] this coefficient was found in two ways: in the semi-classical approximation and from the plot where the inversion frequency was presented as a function of the

reduced mass of hydronium isotopologues. The reduced masses were estimated on the basis of Ref. [20].

We already mentioned above that the accuracy of the semi-classical approach for H_3O^+ is not very high as the action $S \sim 1$. In addition, the answer strongly depends on the value of E_0 in Eq. (9). Here we found E_0 solving an eigenvalue problem for Eq. (3), while in Ref. [15] E_0 was extracted from Ref. [20] to be approximately equal to 400 cm^{-1}. The second, graphical method used in [15] strongly depends on the values of the reduced masses, which were approximately determined from Ref. [20]. These approximations caused overestimation of the Q-factor.

Here, in order to improve the accuracy, we have done numerical calculations within the simple one-dimensional model described above. Optimizing parameters of the potential $U(x)$ we were able to reproduce the experimental low-lying energy levels (the first set of the parameters) and the transition frequency and the barrier height (the second set of the parameters) with an accuracy better than 1%. However, we still estimate the accuracy of this simple model for the Q-factors to be about 5%.

D. Sensitivity coefficients for mixed transitions

Sensitivity coefficients for mixed inversion-rotational transitions in H_3O^+ were considered in [15]. Here we extend this discussion to all four isotopologues of hydronium. Rotational motion is described by the Hamiltonian of the non-rigid asymmetric top. We write it in the basis set $|J, K, s\rangle$ of the oblate symmetric top ($K \equiv K_C$). Additional quantum number s corresponds to the symmetric ($s = +$) and asymmetric ($s = -$) inversion state. Rotational parameters A^s, B^s, and C^s depend on the quantum number s. This dependence contributes to the inversion transition $+ \leftrightarrow -$ and can be considered as centrifugal corrections to the inversion frequency F.

The effective inversion-rotational Hamiltonian is diagonal in quantum numbers J and s and mixes states with K and $K \pm 2$. Matrix elements diagonal in K have the form:

$$H_{K,K} = -\frac{s}{2}F \tag{10a}$$

$$+ \frac{1}{2}(A^s + B^s)\left[J(J+1) - K^2\right] + C^s K^2 \tag{10b}$$

$$+ \Delta_J\left[J(J+1)\right]^2 - \Delta_{KJ}J(J+1)K^2 - \Delta_K K^4, \tag{10c}$$

where the last three terms describe centrifugal corrections to rigid rotor. Matrix elements nondiagonal in K are given by:

$$H_{K,K+2} = \frac{1}{4}(A^s - B^s)\left[J(J+1) - K(K+1)\right]^{1/2}$$
$$\times \left[J(J+1) - (K+1)(K+2)\right]^{1/2}. \tag{10d}$$

Effective Hamiltonian (10) has ten parameters, which have to be fitted to the experimental spectrum. For

the symmetric species we require that $A^s = B^s$ and $\Delta_{KJ} = 0$, leaving seven free parameters. Such fits were done for H_3O^+ in Ref. [24], for H_2DO^+ in [20, 25, 26], for HD_2O^+ in [27, 28], and for D_3O^+ in [29]. In the cited literature the centrifugal terms (10c) are also assumed to depend on s. These s-dependent corrections appear to be much smaller than all other parameters of the effective Hamiltonian and here we reduce the number of free parameters by neglecting them.

In order to calculate sensitivity coefficients for mixed transitions we need to specify how parameters of the effective Hamiltonian depend on μ. The inversion transition energy is given by the parameter F, whose dependence on μ was discussed in Sec. II C. Averaged rotational constants A, B, and C depend on the respective moments of inertia and are, therefore, proportional to μ ($A = (A^+ + A^-)/2$, etc.). Centrifugal parameters Δ_i appear in the second order of adiabatic perturbation theory and are quadratic in μ.

It is more difficult to determine the μ-dependence of the differences $A^+ - A^-$, $B^+ - B^-$, and $C^+ - C^-$, which present centrifugal corrections to the inversion transition energy F. All of them must have the same dependence on μ, so we will consider only $W_K \equiv C^+ - C^-$.

Clearly, the rotational constant C generally depends on the inversion coordinate: $C = C_0 + C_1 x^2 + \dots$. This generates a correction to the inversion potential (4), $U(x) \to U(x) + C_1 x^2 K^2$. To a first approximation we can substitute x with its equilibrium value $x_{\min}$. Consequently, $U_{\min} \to U_{\min} + C_1 x_{\min}^2 K^2$. We can now use Eq. (8) to estimate the respective change in inversion frequency $\omega_{\text{inv}} \to \omega_{\text{inv}} + W_K K^2$. After some algebra we arrive at:

$$W_K = \omega_{\text{inv}} \frac{S}{\Delta U - E_0} C_1 x_{\min}^2. \tag{11}$$

Differentiating this expression in respect to μ we get:

$$\frac{\delta W_K}{W_K} = \left(Q_{\mu,\text{inv}} + \frac{1}{2}\right)\frac{\delta\mu}{\mu}. \tag{12}$$

We conclude that centrifugal corrections to inversion frequency scale as $\mu^{Q_{\mu,\text{inv}}+1/2}$, which is sufficiently close to the estimate [6].

Since we determined how the parameters of the effective Hamiltonian depended on μ, we can find the sensitivity of the mixed transitions by numerical differentiation of the eigenvalues of the effective Hamiltonian. Results of these calculations are listed in Tables IV and V. Note that if we neglect all centrifugal corrections, we can write the approximate expressions for the frequency and the sensitivity of the mixed inversion-rotational transition [14]:

$$\omega_{\text{mix}} = \omega_r \pm \omega_{\text{inv}}, \tag{13a}$$

$$Q_{\mu,\text{mix}} = \frac{\omega_r}{\omega_{\text{mix}}} \pm Q_{\mu,\text{inv}}\frac{\omega_{\text{inv}}}{\omega_{\text{mix}}}. \tag{13b}$$

For small values of the quantum numbers J and K considered here the centrifugal corrections are small and approximation (13) is rather good.

TABLE IV: Sensitivities of the low frequency mixed inversion-rotational transitions in symmetric isotopologues of hydronium. Molecular states are labeled with quantum numbers J_K^s. Error bars for sensitivity coefficients Q_μ correspond to the errors for inversion transitions in Table III.

Transition		Frequency (MHz)		Q_μ
Upper	Lower	Theory	Exper.	
H_3O^+				
1_1^-	2_1^+	307072	307192.4	6.4(5)
3_2^+	2_2^-	365046	364797.4	−3.5(5)
3_1^+	2_1^-	389160	388458.6	−3.1(4)
3_0^+	2_0^-	397198	396272.4	−3.0(4)
0_0^-	1_0^+	984690	984711.9	2.7(2)
4_3^+	3_3^-	1031664	1031293.7	−0.6(2)
4_2^+	3_2^-	1071154	1069826.6	−0.5(2)
3_2^-	3_2^+	1621326	1621739.0	2.0(1)
2_1^-	2_1^+	1631880	1632091.0	2.0(1)
1_1^-	1_1^+	1655832	1655833.9	2.0(1)
D_3O^+				
3_1^-	3_1^+	450608	450709.7	2.7(1)
3_2^-	3_2^+	454910	454940.3	2.7(1)
2_1^-	2_1^+	456194	456211.4	2.7(1)
1_1^-	1_1^+	459918	459917.7	2.7(1)
2_2^-	2_2^+	460496	460493.1	2.7(1)
3_3^-	3_3^+	462080	462074.6	2.7(1)
0_0^-	1_0^+	120117		7.5(4)
2_1^+	1_1^-	220408		−2.5(2)
2_0^+	1_0^-	221782		−2.5(2)

TABLE V: Sensitivities of the low frequency mixed inversion-rotational transitions in asymmetric isotopologues of hydronium. Molecular states are labeled with quantum numbers J_{K_A,K_C}^s.

Transition		Frequency (MHz)		Q_μ
Upper	Lower	Theory	Exper.	
H_2DO^+				
$3_{1,2}^+$	$2_{0,2}^-$	210994	211108.8	−5.9(6)
$1_{0,1}^-$	$2_{1,1}^+$	250920	250914.1	6.8(5)
$3_{2,1}^+$	$2_{1,1}^-$	312737	312831.8	−3.6(4)
$3_{2,2}^+$	$2_{1,2}^-$	412156	412130.2	−2.5(3)
$3_{3,0}^+$	$2_{2,0}^-$	632799	632901.7	−1.2(2)
$3_{3,1}^+$	$2_{2,1}^-$	649742	649653.4	−1.2(2)
$0_{0,0}^-$	$1_{1,0}^+$	673229	673257.0	3.2(2)
$4_{2,2}^+$	$3_{1,2}^-$	715955	715827.9	−1.0(2)
$4_{1,3}^+$	$3_{0,3}^-$	716961	716959.4	−1.0(2)
$1_{1,1}^-$	$2_{2,1}^+$	6633		219(18)
$1_{1,0}^-$	$2_{2,0}^+$	51108		29(2)
HD_2O^+				
$0_{0,0}^-$	$1_{1,0}^+$	380753	380538.0	4.0(2)
$3_{2,2}^+$	$2_{1,2}^-$	474792	474541.1	−1.4(2)
$5_{2,3}^-$	$5_{3,3}^+$	525419	525451.5	3.1(2)
$3_{3,0}^+$	$2_{2,0}^-$	610712	610573.1	−0.8(1)
$3_{3,1}^+$	$2_{2,1}^-$	626907	627069.8	−0.8(2)
$6_{2,4}^-$	$6_{3,4}^+$	632532	632776.9	1.9(1)
$3_{1,2}^+$	$3_{2,2}^-$	634305	633793.2	2.8(1)
$4_{1,3}^-$	$4_{2,3}^+$	707925	707552.6	2.6(1)
$1_{0,1}^-$	$1_{1,1}^+$	728086	728420.2	2.6(1)
$1_{0,1}^-$	$2_{1,1}^+$	35047		33(2)
$2_{2,0}^+$	$1_{1,0}^-$	93734		−11(1)
$2_{2,1}^+$	$1_{1,1}^-$	129633		−7.7(6)

III. DISCUSSION

Our final results for sensitivity coefficients for inversion-rotational transitions between low-lying states of all hydronium isotopologues are listed in Tables IV and V. There we also give calculated frequencies and experimental frequencies, where known (see Refs. [25, 28–30]). The errors for the Q-factors correspond to the uncertainties in Table III. For low-frequency mixed transitions the errors are increased due to cancelations between rotational and tunneling contributions in Eq. (13b). For the experimentally observed transitions we use experimental frequencies to calculate Q-factors. For unknown transitions we have to use predicted values. The accuracy of our model with limited number of centrifugal corrections decrease with increasing rotational energy. For given J the latter is smaller for heaviest isotopologue. Therefore, the accuracy of the model is highest for D_3O^+ (~ 100 MHz) and lowest for H_3O^+, where the maximum error is almost 1 GHz. However, the errors in Q-factors from the inaccuracy in frequency do not exceed 2% and can be neglected compared to the error associated with $Q_{\mu,\mathrm{inv}}$.

It is clear from Eq. (13) that mixed transitions can have high sensitivities only if $|\omega_{\mathrm{mix}}| \ll \omega_{\mathrm{inv}}$ [note, that (13a) allows negative frequencies ω_{mix}]. Thus, we are primarily interested in transitions from the microwave range and low-frequency submillimeter transitions. One can see from Tables IV and V, that all isotopologues have such transitions with both positive and negative sensitivities, whose absolute values are significantly larger than unity.

The lowest frequency 6.6 GHz corresponds to the transition $1_{1,1}^- \rightarrow 2_{2,1}^+$ in H_2DO^+. This frequency is 184 times smaller than respective inversion frequency. Consequently, the sensitivity coefficient for this transition is close to two hundred. Other frequencies are at least an order of magnitude larger and respective sensitivities are much smaller.

As we pointed out above, our present value of $Q_{\mu,\mathrm{inv}}$ for H_3O^+ is 20% smaller than that in Ref. [15]. Consequently, the absolute values of our Q-factors for mixed transitions are also significantly smaller. Still, the difference ΔQ between sensitivities of the 307 GHz line on the one hand and 365 GHz and 396 GHz lines on the other hand is close to 10, or 3 times larger, than ΔQ for ammonia method [6]. These three lines have been observed from the interstellar medium (see [31] and references therein). That makes hydronium very promising candidate for the μ-variation search.

Submillimeter spectra of H_3O^+ are usually observed from warm and dense star forming regions, where hydronium is one of the most abundant molecule [32]. Up to now deuterated hydronium was not observed from the

interstellar medium. However, deuterated isotopologues of ammonia were observed several times [33]. Thus, it is possible that hydronium isotopologues can be found in the future. As we have showed here, this can give additional possibilities to study μ-variation.

IV. ACKNOWLEDGMENTS

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